

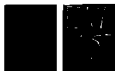
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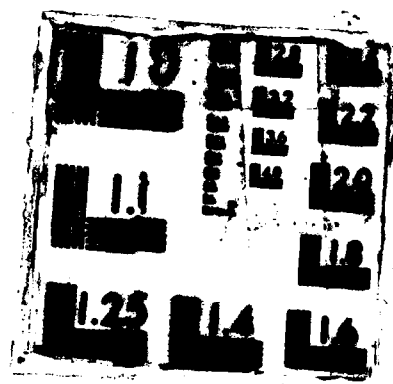
MACROCYCLES CONTAINING TIN THROUGH SPACE COOPERATIVE
BINDING AND HIGH SIZ. (U) TEXAS A AND M UNIV COLLEGE
STATION DEPT OF CHEMISTRY M NEWCOMB ET AL. 27 JUL 87
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Macrocycles Containing Tin. Through Space Cooperative Binding
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by

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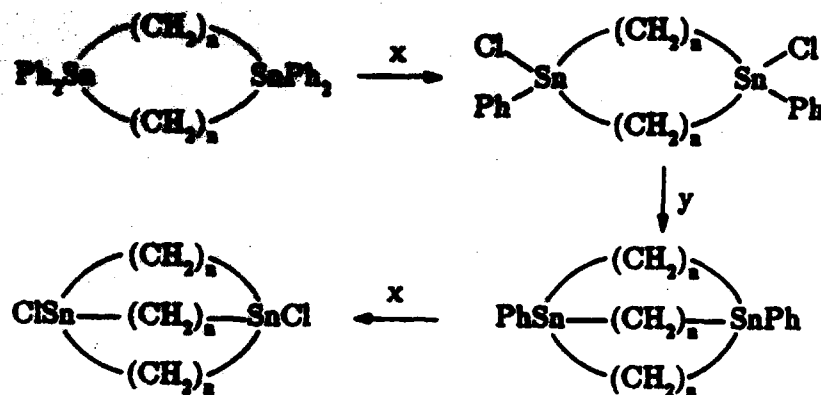


**Macrocycles Containing Tin. Through Space Cooperative Binding
and High Size Selectivity in the Complexation
of Chloride Ion by Lewis Acidic Macrobicyclic Hosts**

The interaction of basic macrocyclic and macrobicyclic hosts with cationic guests has been studied intensively in recent years. In contrast, the analogous complexation of anionic guests by acidic polydentate or macrocyclic hosts has received little attention.¹ Recently, we found low selectivity in binding of chloride ion in organic solvents by a series of macrocyclic hosts containing two Lewis acidic tin atoms.² We anticipated that the addition of more binding sites to or the incorporation of structural rigidity into our Lewis acidic macrocyclic hosts would result in more selective anion complexation. Creation of macrobicycles appeared to be one way to build up binding site rigidity rapidly since Lewis acidic tin atoms containing one electron withdrawing group will complex donors in a trigonal bipyramidal structure with the donor and withdrawing groups in the axial positions.³ In this communication we report Lewis acidic macrobicycles in which both the dynamics and energetics of binding of chloride anion are highly size dependent; this apparently represents selective binding of chloride within the host cavity in a manner directly analogous to the binding of cations by cryptands.⁴

The reaction sequence for preparation of macrobicyclic hosts 1 from macrocycles is shown in the Scheme. The starting macrocycles have been reported⁵ as has the immediate precursor of 1b.⁶ The macrobicyclization reactions were effected in 20-30% yields for the precursors to 1b-1d but only in 4% yield for the (apparently) strained precursor to 1a. The final HCl cleavage reactions were virtually quantitative. Sharp melting products 1 were characterized by ¹H, ¹³C and ¹¹⁹Sn NMR spectroscopy.

Scheme

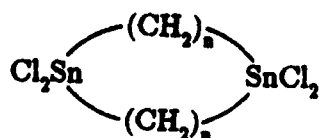


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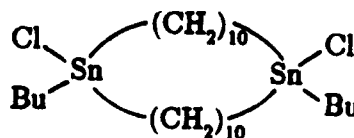
(a: $n = 6$, b: $n = 8$, c: $n = 10$, d: $n = 12$)

Reagents: x, HCl in CH_2Cl_2 ; y, $\text{BrMg}(\text{CH}_2)_n\text{MgBr}$ in THF.

The complexation of chloride by hosts 1 was studied by ^{119}Sn NMR spectroscopy.⁷ Previously, we observed that macrocyclic hosts 2 exchanged chloride fast on the ^{119}Sn NMR time scale and that the first and second binding constants for hosts 2 were nearly the same for each host and varied little between hosts.² In this work, similar behavior was observed for macrocyclic model 3 in the binding of chloride in CDCl_3 solution; addition of increments of tetrahexylammonium chloride to a solution of 3 resulted in a smooth shift for the single sharp peak from +150 ppm (tetra-coordinate) to -50 ppm (penta-coordinate). Thus, model 3 (like hosts 2) binds two chloride ions strongly and equilibrates rapidly ($k > 5 \times 10^6 \text{ s}^{-1}$).



2 ($n = 8, 10, 12$)



3

The ^{119}Sn NMR spectra of bicyclic hosts 1 showed dramatic differences in comparison to those of their macrocyclic counterparts when chloride ion was present. Unlike macrocycles 2 and 3, bicyclic hosts 1b-d in the presence of excess chloride bound only one chloride per host; the limiting chemical shifts were at about the mid-point of the tetra- and penta-coordinate tin shifts (one signal for the two tin atoms arises either from fast exchange within the complex or complexation of chloride by both tin atoms simultaneously). There was no indication that any host 1 bound a second chloride anion. Thus, since the tin atoms are insulated from one another by hydrocarbon chains, there is a through space cooperative binding effect in 1b-d mandated by the structure.

The rates of binding of chloride by hosts 1 were substantially slower than those for cycles 2 and 3. In the presence of 0.5 equivalents of chloride ion per host, the ^{119}Sn NMR spectra of C-12 host 1d at room temperature consisted of one broad signal that increased in broadness at lower temperatures. The spectrum of the C-10 host 1c (plus 0.5 equiv of Cl^-) at room temperature contained one very broad signal, but at -50°C broad signals at $+150$ ppm (uncomplexed) and $+40$ ppm (1:1 complex) were observed. The spectrum of the slower exchanging C-8 host 1b (with 0.5 equiv of Cl^-) contained two sharp signals at -50°C that broadened on warming (Figure).



The binding of chloride by 1b-d is described by the simple model in equation 1. Line shape analyses of the spectra containing hosts 1b-d and chloride gave kinetic results,⁸ some of which are listed in the Table. The rates of complexation and decomplexation were slowed appreciably as the chain length decreased; we presume that this reflects steric interactions as the chloride squeezes between two chains to enter or exit the cavities. For host 1b,

studies of solutions of varying concentration indicated that decomplexation (k_p) was rate limiting; an Arrhenius treatment for this first order decomplexation of chloride from the $(lb \cdot Cl)^-$ complex gave an E_a of 9.1 ± 0.5 kcal/mol. The binding constants of hosts lb and lc at $-20^\circ C$ were nearly an order of magnitude greater than that for host ld; apparently the best cavity size for chloride occurs between hosts lb and lc.

A more dramatic demonstration of size selectivity was found when the C-6 bicycle la was studied. At room temperature the ^{119}Sn NMR spectrum of la (+148 ppm) was unaltered by the addition of excess chloride. The absence of line broadening or a second signal in the +30-40 ppm region in the spectra of la showed that no complexation occurred to the limit of our detection capabilities. With the conservative estimate that even in the most difficult to detect case (slow exchange limit) we would have observed 5% complex if it was present, we can set a limit on K_{eq} for la of $< 1 M^{-1}$. Host la is not Lewis acidic towards chloride!

We have shown that highly selective anion binding in organic solvents is possible with appropriately constructed Lewis acidic hosts even when only two binding sites are available. The selectivity can result from either the exclusion of the guest from an under-sized cavity or the poor fit of the guest within an over-sized cavity. The replacement of chloride on bicycles 1 with a non-labile electron withdrawing group should be expected to give hosts that complex a variety of anionic and neutral basic guests selectively.

Acknowledgment. This work was supported by the Office of Naval Research.

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7. ^{119}Sn NMR spectra of CDCl_3 solutions were recorded on Varian XL-200 (74.6 MHz and XL-400 (149.2 MHz) spectrometers. Gated decoupling was used to suppress NOE. Chemical shifts were measured against internal Me_4Sn .
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9. A two site exchange model was used.¹⁰ The T_2 values used in simulations were determined experimentally (Varian's CPMGT2 sequence) for host 1b at 149.2 MHz (0.05 s for the uncomplexed and 0.003 s for the complexed signal).
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Table. Rates and Equilibrium Constants for Binding Chloride Ion by Hosts 1.^a

Host	Temp (°C)	k_r (s ⁻¹)	k_f (M ⁻¹ , s ⁻¹) ^b	K_{eq} (M ⁻¹)
1b ^c	-50	2.0×10^2	8.9×10^3	44
	-40	3.6×10^2	2.2×10^4	61
	-30	8.4×10^2	3.7×10^4	44
	-20	2.0×10^3	6.6×10^4	33
	-10	4.3×10^3	1.2×10^5	28
1c	-20	3.0×10^4	1.0×10^5	36
1d	-50	5.6×10^4	3.1×10^5	5.5
	-20	3.2×10^5	1.9×10^6	5.9
	20	2.7×10^6	1.2×10^7	4.4

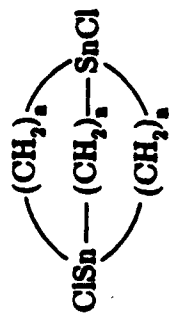
^a Results from line shape analyses of spectra of CDCl₃ solutions containing hosts and tetrahexylammonium chloride.

^b k_f was calculated from the k_f' of the simulation and the concentration of free chloride; values are less accurate than those of k_r , especially in the low temperature studies with 1b where most of the chloride was complexed.

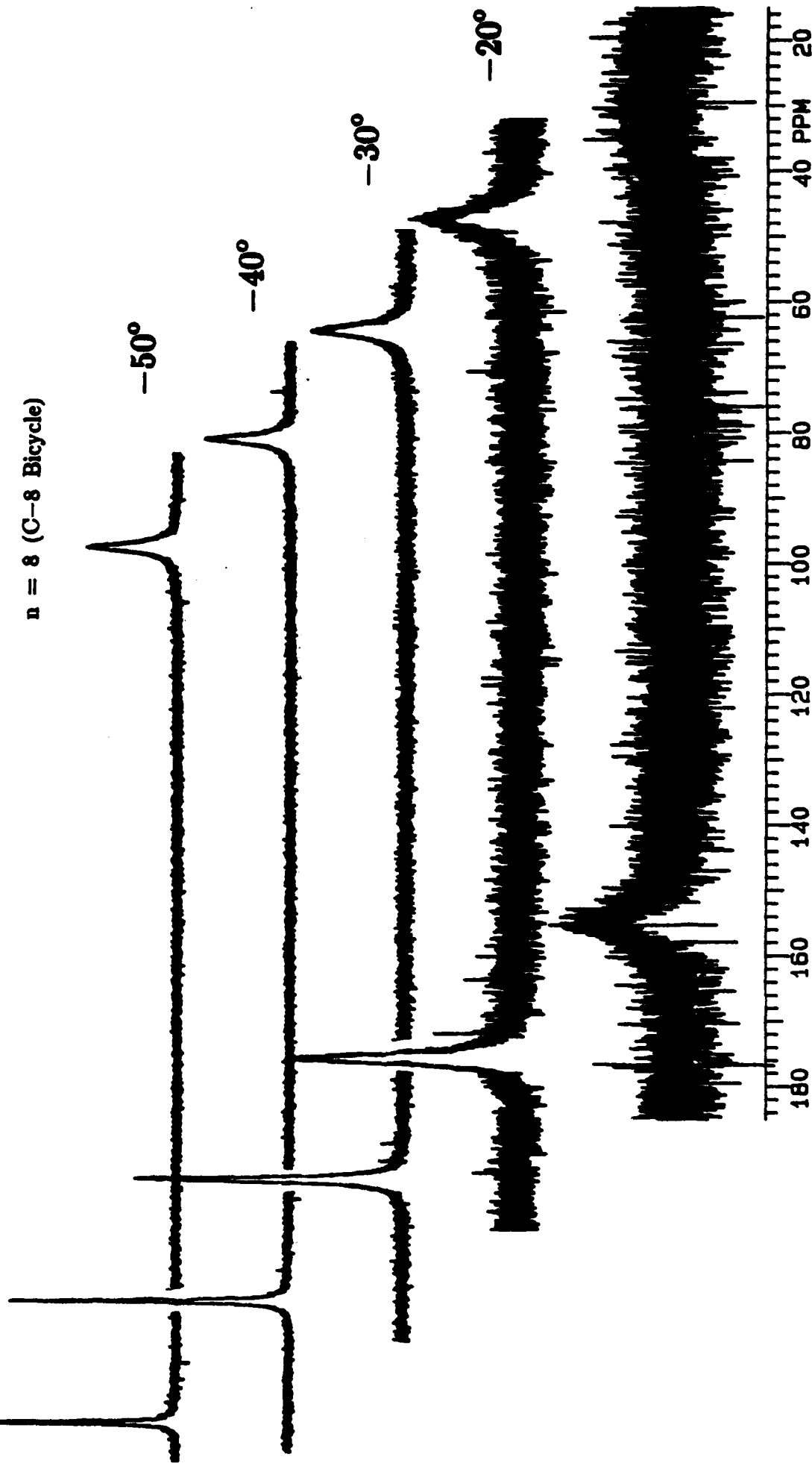
^c Averages of four values for -50 to -30 °C and three values for -20 °C.

Figure ^{119}Sn NMR spectra (149.2 MHz) of a CDCl_3 solution containing host 1b and 0.5 equiv of tetrahexylammonium chloride.

C-8 Bicycle with Chloride
(^{119}Sn NMR, 149 MHz)



n = 8 (C-8 Bicycle)



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